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(71) Applicant *(for all designated States except US)*: VYSOKÁ ŠKOLA CHEMICKO - TECHNOLOGICKÁ [CZ/CZ]; Technická 1905/5, 166 28 Praha 6 (CZ).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: RADA, Miroslav [CZ/CZ]; Americká 247, 345 61 Staňkov (CZ). ŠAŠEK, Ladislav [CZ/CZ]; U Petřin 1858/3, 162 00 Praha 6 (CZ). ŠAŠEK, Ladislav [CZ/CZ]; Mečíkova 2855/2, 106 00 Praha 10 (CZ).

(74) Agent: SMRČKOVÁ, Marie; Ctiradova 1, 140 54 Praha 4 (CZ).

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(54) Title: LEAD-FREE CRYSTAL GLASS WITH THE REFRACTIVE INDEX HIGHER THAN 1,52

(57) Abstract

Lead-free cyrstal glass with the refractive index higher than 1,52, designated for the production of man-made and machine-made utility glass especially of luxurious character with high light transmittance, perfect clearness and elevated hydrolitical resistance which is suitable particularly for decorating by cutting, engraving and other decorating techniques and is well polishable by using both chemical and mechanical processes, containing in % by weight from 50 to 75 of silicon dioxide SiO_2, from 0,05 to 10 of aluminium oxide Al_2O_3, from 0,05 to 15 of zirconium dioxide ZrO_2, from 0,001 to 2,5 of hafnium dioxide HfO_2, from 0,001 to 5 of titanium dioxide TiO_2, from 2 to 9 of calcium oxide CaO, from 0,001 to 6 of magnesium oxide MgO, from 0,05 to 10 of zinc oxide ZnO, from 0,1 to 10 of potassium oxide K_2O, from 5 to 16 of sodium oxide Na_2O, from 0,05 to 2,5 of entimony trioxide Sb_2O_3 and the total amount of iron expressed as iron trioxide Fe_2O_3 ranges from 0,005 to 0,035 % by weight, while this glass further contains in % by weight from 0,001 to 1,25 of sulphates SO_4^{2-} and chlorides Cl^- and from 0,000005 to 0,8105 at least one component from the group comprising erbium oxide Er_2O_3, neodymium oxide Nd_2O_3, ceric oxide CeO_2, cobaltous oxide CoO, nickel oxide NiO, manganese oxides and selenium compounds. In any case, sum of all components mentioned totals at lest 99,6 % by weight.

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Lead-free crystal glass with the refractive index higher than 1,52

Technical field

This invention relates to lead-free crystal glass with the refractive index higher than 1,52 which is intended for the man-made and machine-made utility glassware, especially those of luxurious character, with high lustre and light transmittance. The glass contains silicon dioxide SiO_2, aluminium oxide Al_2O_3, zirconium dioxide ZrO_2, hafnium dioxide HfO_2, titanium dioxide TiO_2, calcium oxide CaO, magnesium oxide MgO, zinc oxide ZnO, potassium oxide K_2O, sodium oxide Na_2O, antimony trioxide Sb_2O_3, iron trioxide Fe_2O_3, sulphates, chlorides and at least one component from the group incorporating erbium oxide Er_2O_3, neodymium oxide Nd_2O_3, ceric oxide CeO_2, cobaltous oxide CoO, nickel oxide NiO, manganese oxides and selenium compounds.

Background art

For the products from so called cheap crystal glass accentuated by a low price the refractory index fluctuates about a value of 1,51 and, barium oxide BaO and lead oxide PbO are being used by some manufacturers but in smaller amounts only, as was stated by A.Smrček in the journal Sklář a keramik 38 , (1988), p. 286-294. The group of special crystal glass types represents already more refined products in which the refractive index is under control and has to be maintained close to the value 1,52. This can be achieved by addition of barium oxide BaO, zinc oxide ZnO and, as the case may be, in smaller amounts even of lead oxide PbO, as it was stated e.g. in DE-patent from 1987 No. 2839645, such a glass according to said patent contains in % by weight as follows: silicon dioxide SiO_2 65 to 75, aluminium oxide Al_2O_3 0,1 to 2, calcium oxide CaO 2 to 12, magnesium oxide MgO 0 to 8, sodium oxide Na_2O 7 to 15,potassium

oxide K_2O 0 to 10, lithium oxide Li_2O 0 to 3, barium oxide BaO 1 to 6, zinc oxide ZnO 0,2 to 3,lead oxide PbO 0 to 10 and titanium dioxide TiO_2 0,2 to 5.This invention covers by its chemical composition, with the exception of titanium dioxide TiO_2 most of crystal glass of types being produced excepting of lead and high-lead crystal glass produced with the content of lead oxide PbO ≥ 24 % by weight.It is also necessary to refer to the published Japanese patent application from 1986 No. 61270234, though relating to glass types for fluorescent lamps, but with the composition analogous to crystal glasses. The glass types according to this invention contain in % by weight from 65 to 75 of silicon dioxide SiO_2, from 1 to 2,5 of aluminium oxide Al_2O_3, from 0,001 to 0,02 of iron trioxide Fe_2O_3, from 10 to 18 of sodium oxide Na_2O, from 0 to 2 of potassium oxide K_2O, while the sum of sodium and potassium oxides ranges between 10 and 18, from 1 to 10 of calcium oxide CaO, from 0,5 to 6 of magnesium oxide MgO, while the sum of calcium and magnesium oxides ranges between 2 an 15, from 0,1 to 2 of barium oxide BaO, from 1 to 3 of boron oxide B_2O_3 and 0,2 to 2 of antimony trioxide Sb_2O_3, while the sum of barium, boron and antimony oxides ranges between 1,4 and 6 % by weight.

For the products of luxurious character which are decorated predominatingly by cutting the lead and high-lead crystal glass types are used where the refractive index value ≥ 1,545 is required.At the present time the unharmful hygienic properties of glass are being preferred particularly concerning the content of lead and barium in the leaching, as important also the purity of the atmosphere and effluents is regarded. With regard to the fact that in the production of those special crystal glass types the refractive index of the desired value is being elevated largely by an increased amount of lead oxide PbO and barium oxide BaO, the said hygiene properties that are required induce hardly solvable problems in the production of such glass types.

The disadvantages mentioned will be improved according to published Czechoslovak patent application No. 1344-91 which

corresponds to European patent application No. 92909183.3, the proposed chemical composition of crystal lead-free glasses conforming with it contains in % by weight from 50 to 65 of silicon dioxide SiO_2, from 0,1 to 10 of aluminium oxide Al_2O_3, from 0,5 to 17 of zirconium dioxide ZrO_2, from 10 to 22 of potassium oxide K_2O and/or sodium oxide Na_2O, from 2 to 10 of calcium oxide CaO and/or magnesium oxide MgO,and from 0,01 to 0,025 of iron trioxide Fe_2O_3, individually or in a combination it contains from 0,1 to 10 % by weight of barium oxide BaO, zinc oxide ZnO, boron oxide B_2O_3 and lithium oxide Li_2O and traces to 1 % by weight of antimony trioxide Sb_2O_3. As further modifiers individually or in a combination titanium dioxide TiO_2 and stannic dioxide SnO_2 are present in the range of traces to 1 % by weight.

The composition of a lead-free zinc-silicon crystal glass is presented also in the published patent application EP from 1991 No. 91121730.5. The glass according to this invention contains in % by weight from 65 to 70 of silicon dioxide SiO_2, from 6 to 9 of calcium oxide CaO, from 4 to 12 of potassium oxide K_2O, from 4 to 12 of sodium oxide Na_2O, from 0,5 to 5 of boron oxide B_2O_3, from 4 to 7 of zinc oxide ZnO, from 0,1 to 1 of antimony trioxide Sb_2O_3 and from 1 to 6 of zirconium dioxide ZrO_2 and/or titanium dioxide TiO_2.

Zirconium dioxide ZrO_2 according to the published Japanese patent application from 1988 No. 63147843 can be used as a component also in a chemically resistent glass which composition in % by weight is as follows: from 63 to 67 of silicon dioxide SiO_2, from 4 to 4,8 of boron oxide B_2O_3,from 4 to 5,5 of aluminium oxide Al_2O_3, from 0 to 4 of titanium dioxide TiO_2, from 2,5 to 3,6 of magnesium oxide MgO, from 4,7 to 8,7 of calcium oxide CaO, from 0 to 5 of barium oxide BaO, from 7,5 to 13,9 of sodium oxide Na_2O, from 0 to 2 of potassium oxide K_2O, while the sum of sodium and potassium oxides ranges from 8 to 15,5, from 0 to 1 of iron trioxide Fe_2O_3 and from 0 to 5 of zirconium dioxide ZrO_2.

The next group is composed of inventions, in which besides zirconium dioxide ZrO_2 also strontium oxide SrO is incorporated. This category according to the U.S. patent from 1977 No. 4065317 includes glasses with a high chemical resistance which are suitable for pharmaceutical purposes, scientific and biological branches. The composition of these glass types is as follows (in mol.%): from 75 to 82 of silicon dioxide SiO_2, from 2 to 8 of zirconium dioxide ZrO_2, from 1 to 5 of aluminium oxide Al_2O_3, from 2 to 10 of sodium oxide Na_2O, from 2 to 10 of potassium oxide K_2O, from 2 to 10 of calcium oxide CaO, from 2 to 10 of strontium oxide SrO, from 2 to 10 of barium oxide BaO, without boron oxide B_2O_3. According to the European patent application from 1991 No. 405579 strontium oxide SrO is used as a component also in packing glass with the composition as follows (in % by weight): from 45 to 70 of silicon dioxide SiO_2, from 5 to 16 of zirconium dioxide ZrO_2, with 10 to 30 of alkaline metal oxides, over 12 oxides of divalent metals, and over 5 oxides of trivalent metals, while as alkaline metals sodium Na, potassium K or lithium Li are being regarded, and magnesium Mg, calcium Ca, strontium Sr, zinc Zn or barium Ba being classified among divalent metals and aluminium Al, iron Fe or boron B among trivalent metals. Strontium oxide SrO acts as a component in packing glass also in USSR patent from 1972 No. 330119. The complete composition is as follows (in % by weight): from 68 to 73 of silicon dioxide SiO_2, from 1,8 to 4,5 of aluminium oxide Al_2O_3, from 0,02 to 1,5 of iron trioxide Fe_2O_3, from 0,5 to 4 of magnesium oxide MgO, from 4 to 9,5 of calcium oxide CaO, from 2 to 5,2 of strontium oxide SrO, from 11 to 13 of sodium oxide Na_2O, from 0,5 to 2 of potassium oxide K_2O and from 0,2 to 2 of zirconium dioxide ZrO_2.

According to the published Japanese application from 1976 No. 51055310 zirconium dioxide ZrO_2 is included in watch covering glasses, the composition of which in % by weight varies in the range between 4 to 10 of aluminium oxide Al_2O_3, 0 to 5 of magnesium oxide MgO, 10 to 20 of sodium oxide Na_2O, 2 to 10 of

potassium oxide K_2O, 0 to 10 of boron oxide B_2O_3 . The actual composition contains (in % by weight): 65 of silicon dioxide SiO_2, 4 of aluminium oxide Al_2O_3, 0,017 of iron trioxide Fe_2O_3, 0,55 of titanium dioxide TiO_2, 0,7 of magnesium oxide MgO, 3,96 of zirconium dioxide ZrO_2, 0,65 of arsenic trioxide As_2O_3, 10 of sodium oxide Na_2O, 9,5 of potassium oxide K_2O, 3,62 of boron oxide B_2O_3 and 3,92 of zinc oxide ZnO.

The lead-free crystal glass types mentioned in the survey according to the Czechoslovak patent application No.1344-91 which corresponds to the European patent application No.92909183.3 are designated for the man-made and machine-made utility glassware of plain type or decorated by engraving, cutting and other decorative techniques. These glass types that are well polishable mainly by chemical processes are suitable above all for cutting by diamond tools.

Disclosure of the invention

This invention relates to the composition of crystal lead-free glass with the refractive index higher than 1,52 contains 50 to 75 % by weight of silicon dioxide SiO_2, 0,05 to 10 % by weight of aluminium oxide Al_2O_3, 0,05 to 15 % by weight of zirconium dioxide ZrO_2, 0,001 to 2,5 % by weight of hafnium dioxide HfO_2, 0,001 to 5 % by weight of titanium dioxide TiO_2, 2 to 9 % by weight of calcium oxide CaO, 0,001 to 6 % by weight of magnesium oxide MgO, 0,05 to 10 % by weight of zinc oxide ZnO, 0,1 to 10 % by weight of potassium oxide K_2O, 5 to 16 % by weight of sodium oxide Na_2O, 0,05 to 2,5 % by weight of antimony trioxide Sb_2O_3 and total content of iron expressed as iron trioxide Fe_2O_3 varies between 0,005 and 0,035 % by weight while this glass further contains 0,0001 to 1,25 % by weight of sulphates SO_4^{2-} and chlorides Cl^- and 0,000005 to 0,8105 % by weight of at least one component from the group including erbium oxide Er_2O_3, neodymium oxide Nd_2O_3, ceric oxide CeO_2, cobaltous oxide CoO, nickel oxide NiO, manganese oxides and selenium compounds. In any case the total of all these components is at

least 99,6 % by weight.

As impurities amounting maximum of 0,4 % by weight the compounds carried in above all by usual glass raw materials can be present such as strontium oxide SrO, lead oxide PbO, cadmium oxide CdO, cupric oxide CuO, arsenic trioxide As_2O_3, praseodymium trioxide Pr_2O_3, samarium oxide Sm_2O_3, chrome oxide Cr_2O_3, vanadic oxide V_2O_5, uranium trioxide UO_3, thorium dioxide ThO_2, fluorides, etc.

Glass refining by antimony trioxide Sb_2O_3 or if needed by antimonitans introduced usually into glass batch in common with nitrates will be more intensive at the presence of sulphates SO_4^{2-} varying between 0,0001 and 0,75 % by weight and chlorides Cl^- between 0,001 and 0,5 % by weight.

High light transmittance and perfect clearness is achieved at the presence at least one component from the group comprising 0,0001 to 0,2 % by weight of erbium oxide Er_2O_3, 0,0001 to 0,2 % by weight of neodymium oxide Nd_2O_3, 0,001 to 0,2 % by weight of ceric oxide CeO_2, 0,000005 to 0,0005 % by weight of cobaltous oxide CoO, 0,00001 to 0,005 % by weight of nickel oxide NiO, 0,001 to O,200 % by weight of manganese oxide MnO_2 expressing in re-count manganese oxides and, selenium amount of 0,00001 to 0,005 % by weight, expressing in re-count selenium compounds.

Utility and technological properties particularly the meltableness and partly also the refractive index of glass, its chemical resistance and the liquidus temperature are advantageously modified by at least one oxide from the group comprising 0,05 to 6 % by weight of barium oxide BaO, 0,001 to 5 % by weight of boron oxide B_2O_3, 0,001 to 1,5 of phosphoric oxide P_2O_5 and 0,001 to 1,5 % by weight of lithium oxide Li_2O.

As further modifiers, with the respect to the refractive index, partly to the mean dispersion and to the surface tension, this glass can contain with advantage at least one oxide from the group comprising 0,05 to 5 % by weight of stannic dioxide SnO_2, 0,05 to 2 % by weight of lanthanum oxide La_2O_3, 0,05 to 10 % by weight of bismuth oxide Bi_2O_3, 0,001 to 0,1 % by weight of

molybdic oxide MoO_3 and 0,001 to 0,5 % by weight of tungstic oxide WO_3.

Among dominant advantages of this glass type belong good cutting and engraving abilities, namely by diamond, carborundum, electrite, etc. tools, good polishing ability by using both chemical and mechanical processes, excellent optical properties, especially high light transmittance and perfect clearness. From the point of view concerning crystal glass types its excellent chemical resistance is also of importance and as favourable the comparable or more advantageous melting, refining, forming and cooling temperatures and also convenient crystallization properties can be regarded. But its major preference consists in the absence of hygienic and environmentally harmful lead oxide. During the melting process do not volatilize environmentally irregular lead oxides and arsenic that are used in the manufacture of lead crystal glasses. As it is completely lead-free and is designated above all for the utility glass and consequently for beverage glass and household use it involves the significant advantage that no undesired and healthy damaging lead oxide will pass over into the leaching.

Examples of carrying out invention

This invention will be explained in more detail in the following examples of carrying out.

Example No.	1	2	3	4
Glass components	content in % by weight			
Silicium dioxide SiO_2	63,883	64,857	63,170	64,363
Aluminium oxide Al_2O_3	0,108	0,117	1,800	0,117
Zirconium dioxide ZrO_2	7,522	6,111	5,820	5,081
Hafnium dioxide HfO_2	0,233	0,189	0,180	2,219
Titanium dioxide TiO_2	0,012	0,010	0,009	0,011
Calcium oxide CaO	5,500	6,500	5,800	6,500
Magnesium oxide MgO	0,087	0,103	4,072	0,103

Zinc oxide ZnO		3,000	5,500	2,500	3,000
Potassium oxide K_2O		6,000	4,000	4,000	4,000
Sodium oxide Na_2O		13,000	12,000	12,000	12,000
Antimony trioxide Sb_2O_3		0,500	0,500	0,500	0,500
Iron content expressed by content of iron trioxide Fe_2O_3		0,015	0,015	0,018	0,015
Sulphates SO_4^{2-}		0,004	0,003	0,003	0,004
Chlorides Cl^-		0,086	0,029	0,078	0,043
Erbium oxide Er_2O_3		0,040	–	0,042	0,044
Neodymium oxide Nd_2O_3		0,010	–	0,008	–
Cobaltous oxide CoO		0,00003	0,00005	0,00003	0,00004
Manganese oxides expressed by content of manganese oxide MnO_2		–	0,066	–	–
Boron oxide B_2O_3		–	–	–	2,000
Σ components		100,000	100,000	100,000	100,000
Refractive index at 589,3 nm		1,5469	1,5456	1,5454	1,5450
$t_{\log\eta=2}$	[°C]	1444	1470	1447	1426
$t_{\log\eta=3}$	[°C]	1202	1222	1219	1194
$t_{\log\eta=4}$	[°C]	1050	1068	1076	1050
$t_{\log\eta=7,65}$	[°C]	765	776	803	774
$t_{\log\eta=13}$	[°C]	578	585	620	593
$t_{\log\eta=14,5}$	[°C]	542	550	587	558
$t_{liquidus}$	[°C]	930	960	960	915
hydrolitical resistance in ml [C=0,01mol.l^{-1}] HCl		0,60	0,40	0,40	0,32

Example No.	5	6	7	8
Glass components	content in % by weight			
Silicium dioxide SiO_2	70,739	61,632	64,015	71,497
Aluminium oxide Al_2O_3	2,000	0,063	0,065	0,125
Zirconium dioxide ZrO_2	0,970	6,275	7,178	1,096
Hafnium dioxide HfO_2	0,030	1,225	0,222	0,034
Titanium dioxide TiO_2	0,027	1,000	0,011	0,027
Calcium oxide CaO	7,640	6,000	5,000	6,640
Magnesium oxide MgO	0,020	0,016	0,013	0,018
Zinc oxide ZnO	1,500	1,500	5,000	3,500
Potassium oxide K_2O	3,400	5,800	4,500	3,600
Sodium oxide Na_2O	12,570	13,000	12,000	12,570
Antimony trioxide Sb_2O_3	0,600	0,500	0,500	0,600
Iron content expressed by content of iron trioxide Fe_2O_3	0,008	0,008	0,010	0,008
Sulphates SO_4^{2-}	0,225	0,300	0,003	0,225
Chlorides Cl^-	0,043	0,131	0,040	0,038
Erbium oxide Er_2O_3	0,020	0,050	0,085	0,022
Neodymium oxide Nd_2O_3	0,008	–	–	–
Ceric oxide CeO_2	–	–	0,008	–
Cobaltous oxide CoO	0,000015	0,00005	–	0,00002
Nickel oxide NiO	–	–	–	0,0003
Boron oxide B_2O_3	–	–	1,000	–
Lithium oxide Li_2O	0,200	–	–	–
Stannic dioxide SnO_2	–	0,500	–	–
Bismuth oxide Bi_2O_3	–	2,000	–	–
Molybdic oxide MoO_3	–	–	0,050	–
Tungstic oxide WO_3	–	–	0,300	–
Σ components	100,000	100,000	100,000	100,000
Refractive index at 589,3 nm	1,5204	1,5519	1,5408	1,5200

$t_{\log\eta=2}$	[°C]	1466	1423	1453	1473
$t_{\log\eta=3}$	[°C]	1194	1191	1209	1200
$t_{\log\eta=4}$	[°C]	1027	1046	1057	1032
$t_{\log\eta=7,65}$	[°C]	717	770	769	721
$t_{\log\eta=13}$	[°C]	520	588	581	523
$t_{\log\eta=14,5}$	[°C]	484	555	547	487
$t_{liquidus}$	[°C]	920	895	897	920
hydrolitical resistance in ml [C=0,01mol.l^{-1}] HCl		0,51	0,75	0,34	0,62

In examples carrying out corresponds $t_{\log\eta=2}$ to the melting temperature, $t_{\log\eta=4}$ to the working temperature, $t_{\log\eta=7,65}$ to the softening point temperature, $t_{\log\eta=13}$ to the upper annealing temperature and $t_{\log\eta=14,5}$ to the lower annealing temperature.

The values of hydrolitical resistance expressed in the consumption of 0,01 molar hydrochloric acid in mililitres show that all glasses mentioned fulfil the condition desired for classification in the third class of hydrolitical resistance. By rising the amount of zirconium dioxide ZrO_2, hafnium dioxide HfO_2 and zinc oxide ZnO in glasses mentioned the condition is given for the classification in the second class of hydrolitical resistance.

The given composition of lead-free glass types according to this invention can be also applied into basic composition of coloured glass types that are coloured by using usual procedures and known types of colouring substances and their combinations in current concentrations as well.

Industrial applicability

The lead-free crystal glass with the refractive index higher than 1,52 according to this invention is assigned to the production of man-made and machine-made utility glass, for the products of luxurious character in plain but especially decorated designs using engraving, cutting and further decorative techniques. This type of glass is suitable for processing by diamond, carborundum, electrite, atc. tools, it is well polishable by chemical and mechanical treatment and features a high light transmittance and perfect clearness. It can be applied as initial basis for coloured glass types. This glass is hygienic unharmful concerning the content of detrimental substances in the leaching and by its brilliance can compete with the products made of lead crystal glass.

In question is the production of glass objects used in households and restaurants, e.g. small cups, tumblers, carafes, bowls and, vessels of various shapes and sizes used for decorative purposes such as vases, dishes, etc., including applied art designs and objects of art.

Claims

1. Lead-free crystal glass with the refractive index higher than 1,52 suitable especially for production of man-made and machine-made utility glass containing silicon dioxide SiO_2, aluminium oxide Al_2O_3, zirconium dioxide ZrO_2, hafnium dioxide HfO_2, titanium dioxide TiO_2, calcium oxide CaO, magnesium oxide MgO, zinc oxide ZnO, potassium oxide K_2O, sodium oxide Na_2O, antimony trioxide Sb_2O_3, iron trioxide Fe_2O_3, sulphates, chlorides and at least one component from the group including erbium oxide Er_2O_3, neodymium oxide Nd_2O_3, ceric oxide CeO_2, cobaltous oxide CoO, nickel oxide NiO, manganese oxides and selenium compounds, characterized by its composition, with the content 50 to 75 % by weight of silicon dioxide SiO_2, 0,05 to 10 % by weight of aluminium oxide Al_2O_3, 0,05 to 15 % by weight of zirconium dioxide ZrO_2, 0,001 to 2,5 % by weight of hafnium dioxide HfO_2, 0,001 to 5 % by weight of titanium dioxide TiO_2, 2 to 9 % by weight of calcium oxide CaO, 0,001 to 6 % by weight of magnesium oxide MgO, 0,05 to 10 % by weight of zinc oxide ZnO, 0,1 to 10 % by weight of potassium oxide K_2O, 5 to 16 % by weight of sodium oxide Na_2O, 0,05 to 2,5 % by weight of antimony trioxide Sb_2O_3, the total amount of iron expressed as iron trioxide Fe_2O_3 being ranged from 0,005 to 0,035 % by weight, while this glass further contains 0,0001 to 1,25 % by weight of sulphates SO_4^{2-} and chlorides Cl^- and 0,000005 to 0,8105 % by weight of at least one component from the group comprising erbium oxide Er_2O_3, neodymium oxide Nd_2O_3, ceric oxide CeO_2, cobaltous oxide CoO, nickel oxide NiO, manganese oxides and selenium compounds, the total of all components mentioned being at least 99,6 % by weight.

2. Crystal lead-free glass with the refractive index higher than 1,52 according to claim 1, characterized by its composition, with the content of 0,0001 to 0,75 % by weight of sulphates

SO_4^{2-} and 0,001 to 0,5 % by weight of chlorides Cl^-.

3. Crystal lead-free glass with the refractive index higher than 1,52 according to claims 1 and 2, characterized by its composition, with the content at least of one component from the group comprising 0,0001 to 0,2 % by weight of erbium oxide Er_2O_3, 0,0001 to 0,2 % by weight of neodymium oxide Nd_2O_3, 0,001 to 0,2 % by weight of ceric oxide CeO_2, 0,000005 to 0,0005 % by weight of cobaltous oxide CoO, 0,00001 to 0,005 % by weight of nickel oxide NiO, 0,001 to 0,200 % by weight of manganese oxide MnO_2 expressing in re-count manganese oxides and 0,00001 to 0,005 % by weight of selenium expressing in re-count selenium compounds.

4. Crystal lead-free glass with the refractive index higher than 1,52 according to claims 1 to 3, characterized by its composition, with the content at least of one oxide from the group comprising 0,05 to 6 % by weight of barium oxide BaO, 0,001 to 5 % by weight of boron oxide B_2O_3, 0,001 to 1,5 % by weight of phosphoric oxide P_2O_5 and 0,001 to 1,5 % by weight of lithium oxide Li_2O.

5. Crystal lead-free glass with the refractive index higher than 1,52 according to claims 1 to 3 or according to claims 1 to 4, characterized by its composition, with the content at least one component from the group comprising 0,05 to 5 % by weight of stannic dioxide SnO_2, 0,05 to 2 % by weight of lanthanum oxide La_2O_3, 0,05 to 10 % by weight of bismuth oxide Bi_2O_3, 0,001 to 0,1 % by weight of molybdic oxide MoO_3 and 0,001 to 0,5 % by weight of tungstic oxide WO_3.

INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/CZ 93/00027

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C3/087 C03C3/095 C03C3/11

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 564 802 (SCHOTT GLASSWERKE) 13 October 1993 see page 3, line 21 - page 4, line 39	1-5
A	WO,A,92 19559 (VYSOKÁ SKOLA CHEMICKO-TECHNOLOGICKÁ ÚSTAV SKLA Y KERAMIKY) 12 November 1992 cited in the application see page 2, line 36 - page 4, line 8	1-5
A	EP,A,0 547 263 (INN CRYSTAL GLASS GMBH) 23 June 1993 cited in the application see page 2, line 26 - page 3, line 46	1-5
A	EP,A,0 553 586 (COMPAGNIE DES CRISTALLERIES DE BACCARAT) 4 August 1993 see page 2, line 28 - page 3, line 45	1-5

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 June 1994	29. 06. 94

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Van Bommel, L

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INTERNATIONAL SEARCH REPORT

...formation on patent family members

Intern. ...al Application No
PCT/CZ 93/00027

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0564802	13-10-93	DE-A-	4303474	14-10-93
		JP-A-	6009241	18-01-94
		PL-A-	298472	27-12-93
		SI-A-	9300193	31-12-93
WO-A-9219559	12-11-92	NONE		
EP-A-0547263	23-06-93	NONE		
EP-A-0553586	04-08-93	AU-B-	3635293	13-09-93
		DE-D-	69200011	14-10-93
		DE-T-	69200011	03-03-94
		WO-A-	9316964	02-09-93